

11/02/95

JCO3 Rec'd PCT/PTC 09/890871 07 AUG 2001

## SPECIFICATION

### HYDROTHERMAL ELECTROLYTIC APPARATUS AND PROCESSES

#### FIELD OF THE INVENTION

The present invention relates to apparatus and  
5 processes for performing hydrothermal reaction and  
electrolysis at the same time. As used herein,  
hydrothermal electrolysis means that hydrothermal reaction  
and electrolysis are performed at the same time. According  
to the present invention, a large amount of influent  
10 containing reducible substances such as organics (including  
synthetic polymers) and ammonia, eg, organic waste liquors  
or various industrial waste liquors containing a halide ion  
can be continuously treated.

#### PRIOR ART

15 International Application PCT/JP 98/03544 filed  
August 10, 1998 (International Publication WO99/07641)  
discloses hydrothermal electrolytic processes and apparatus  
previously developed by us. According to these processes  
and apparatus, reducible substances such as organics  
20 (including synthetic polymers) or ammonia can be effec-  
tively oxidatively degraded by performing hydrothermal  
reaction and electrolysis at the same time. When an  
oxidizer or a strong acid ion such as a halide ion is  
contained in the influent, hydrogen emission can be  
25 inhibited in hydrothermal electrolysis. The disclosure of  
International Application PCT/JP 98/03544 is incorporated  
herein as a whole as reference.

In hydrothermal electrolysis, a closed pressure-

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resistant vessel is typically used as a reaction vessel because a high pressure environment is required. Thus, a batch process or a semi-continuous or continuous process consisting of repeated batch processes is applied when  
5 waste liquor is to be clarified by hydrothermal electrolysis.

However, only a small amount of waste liquor could be treated at a time and it was difficult to treat a large amount of waste liquor by a batch process or a semi-  
10 continuous process. For example, it is necessary to supply waste liquor and replace treated effluent each time in the case of a batch process. However, the operation for bolting a flange or the like requires labor and care in order to perform a reaction at high temperature and high  
15 pressure. These processes are inefficient in terms of operating time or running costs.

When waste liquor is to be continuously treated, a large amount of electric power must be supplied in proportion to the amount of waste liquor. Especially when  
20 a large amount of high-load influent is to be continuously treated, a quite large amount of electric power must be supplied, which may sometimes correspond to several thousands to several tens of thousands of amperes of dc. However, it is sometimes difficult to apply several  
25 hundreds to several thousands of amperes of dc, considering that the permissive current density has a limitation depending on the electrode material. As the reaction vessel becomes larger, it also becomes more difficult to

homogeneously supply electric power on the electrode surface to homogeneously advance the reaction.

Therefore, an object of the present invention is to provide a hydrothermal electrolytic apparatus capable of efficiency and continuously treating a large amount of waste liquor.

As a result of examinations to solve the above problems, we found that a large amount of waste liquor can be efficiently treated by increasing the surface area of electrodes in a high-pressure vessel.

#### DISCLOSURE OF THE INVENTION

An aspect of the present invention provides a hydrothermal electrolytic apparatus comprising a reaction cell for electrolyzing an influent containing water and reducible substances at high temperature and high pressure, wherein said reaction cell defines a chamber and has a pair of electrodes and the overall surface area of said pair of electrodes exposed in said chamber per 1 m<sup>3</sup> of the volume of said chamber in said reaction cell is 0.05 m<sup>2</sup> or more.

Preferably, the hydrothermal electrolytic apparatus of the present invention has an inlet at the bottom of the reaction cell for introducing an influent and an outlet at the top for discharging an effluent. This facilitates continuous treatment of influents.

Preferably, said reaction cell comprises two or more tubular reaction cells each having a metal inner wall serving as a cathode, and an anode is provided in each of said reaction cell. The anode and the cathode can form

said pair of electrodes.

Alternatively, said pair of electrodes preferably have a first electrode having two or more concentrically cylindrical first side walls and a first connecting member  
5 for connecting said first side walls together, and a second electrode having two or more concentrically cylindrical second side walls and a second connecting member for connecting said second side walls together, wherein said first side walls of said first electrode and said second  
10 side walls of said second electrode are alternately arranged to form a channel for influent between said first side walls and said second side walls.

Moreover, the hydrothermal electrolytic apparatus of the present invention preferably further has a high-  
15 pressure pump, an influent line for supplying influent to said reaction cell, an oxidizer line for supplying an oxidizer to said reaction cell, and an effluent line for discharging effluent from said reaction cell.

Another aspect of the present invention provides a  
20 process for preparing clarified water, comprising the steps of introducing an influent containing water and reducible substances into a reaction cell of said hydrothermal electrolytic apparatus, supplying a direct current into said reaction cell at a temperature of 100°C or more but  
25 the critical temperature of said influent or less and at a pressure that allows water in said influent to be kept in the liquid phase, and discharging an effluent from said reaction cell. This clarified water may be recycled to

another process or discharged to the environment.

Preferred embodiments of the present invention are explained in detail below with reference to the attached drawings.

5 BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a longitudinal sectional view showing the inner structure of the reaction vessel forming the core of a hydrothermal electrolytic apparatus according to a first embodiment of the present invention.

10 FIG. 2 is a cross-sectional view showing the inner structure of the reaction vessel.

FIG. 3 is an enlarged sectional view of B in FIG. 1.

FIG. 4 is an enlarged cross-sectional view showing a partial inner structure of C in FIG. 1.

15 FIG. 5 is a longitudinal sectional view showing the inner structure of the reaction vessel forming the core of a hydrothermal electrolytic apparatus according to a second embodiment of the present invention.

20 FIG. 6 is a cross-sectional view showing the inner structure of the reaction vessel.

FIG. 7 is an enlarged sectional view of E in FIG. 5.

FIG. 8 is an enlarged sectional view of F in FIG. 6.

FIG. 9 is an enlarged sectional view of G in FIG. 5.

25 FIG. 10 shows a variant of the first embodiment of the present invention.

FIG. 11 is a cross-sectional view showing the inner structure of the reaction vessel in the variant of the first embodiment of the present invention shown in FIG. 10.

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FIG. 12 shows another variant of the first embodiment of the present invention.

FIG. 13 is a schematic view of a hydrothermal electrolytic treatment system of the present invention.

5        FIG. 14 is a schematic view of a hydrothermal electrolytic treatment system according to a third aspect of the present invention.

FIG. 15 is a schematic view of the experimental apparatus for a hydrothermal electrolytic process of the  
10        present invention used in Example 1.

#### THE MOST PREFERRED EMBODIMENTS OF THE INVENTION

Fig. 1 is a longitudinal sectional view showing the inner structure of reaction vessel 1 forming the core of the hydrothermal electrolytic apparatus according to a  
15        first embodiment of the present invention, Fig. 2 is a widthwise sectional view showing the inner structure of the reaction vessel. Fig. 3 is an enlarged sectional view of B in Fig. 1. Fig. 4 is an enlarged sectional view of C in Fig. 2. Fig. 4 shows a section of the part at which a  
20        spacer 43 is provided.

As shown in Figs. 1-4, the hydrothermal electrolytic apparatus according to this embodiment comprises a reaction cell 31 for electrolyzing an influent containing water at high temperature and high pressure. Reaction cell 31  
25        defines chambers 7 and has a pair of electrodes 31a, 41. Thus, the inner face of reaction cell 31 can serve as electrode 31a. The overall surface area of a pair of electrodes 31a, 41 exposed in chamber 7 in reaction cell 31

per 1 m<sup>3</sup> of the volume of the chamber is 0.05 m<sup>2</sup> or more, preferably 0.1 m<sup>2</sup> or more, more preferably 0.2 m<sup>2</sup> or more. The "overall surface area of electrodes" here means the effective surface area of electrodes substantially participating in electrolytic reaction.

If the overall surface area of a pair of electrodes 31a, 41 is less than 0.05 m<sup>2</sup>, enough electric power can not be supplied to the influent for rapid hydrothermal electrolysis.

10 In the first embodiment of the present invention shown in Fig. 1, the reaction cell consists of two or more tubular reaction cells 31. Each of reaction cells 31 has a metal inner wall 31a serving as a cathode and a discharge electrode 41 serving as an anode is provided in each of  
15 said reaction cells 31.

The first embodiment of the present invention comprises a reaction vessel 1. Reaction vessel 1 comprises a lower vessel part 2, a middle vessel part 3 and an upper vessel part 4. Lower vessel part 2 comprises an inlet 21  
20 for introducing influent, an oxidizer inlet 22 for introducing an oxidizer, and a mixing chamber 23 for mixing the influent introduced from inlet 21 with the oxidizer introduced from oxidizer inlet 22. Middle vessel part 3 comprises reaction cells 31 in which the influent mixed  
25 with an oxidizer is electrolyzed under pressure and heating.

Upper vessel part 4 comprises a current feed terminal 42 corresponding to each reaction cell 31. Current feed terminal 42 preferably has an insulating member from

reaction vessel 1. Each current feed terminal 42 has a discharge electrode 41 extending to the inside of reaction cell 31.

Lower vessel part 2, middle vessel part 3 and upper vessel part 4 are connected together via gaskets 5, which tightly seal the inside. Thus, reaction vessel 1 as a whole forms a pressure-resistant vessel.

Each of inlet 21 and oxidizer inlet 22 is singly provided in a wall portion 2a on the bottom of lower vessel part 2. Inlet 21 is connected to an influent line and oxidizer inlet 22 is connected to an oxidizer line.

Mixing chamber 23 is partitioned by a dispersion plate 24 and contains a stirrer 25 therein. Dispersion plate 24 may be any known means for mixing the influent by disturbing the flow. Stirrer 25 is a common type having stirring blades 25a and used to help mixing and connected to a motor not shown.

At the connection between lower vessel part 2 and middle vessel part 3 is provided an introducing chamber 6 for smoothly introducing the influent mixed with an oxidizer in mixing chamber 23 into reaction cell 31. Wall 3a of middle vessel part 3 is connected to a negative line 32, which is in turn connected to a negative terminal not shown of a dc source at constant current and voltage.

The tubular body forming reaction cell 31 is electrically connected with wall 3a of middle vessel part 3. For example, a stainless steel tube may be welded to a stainless steel middle vessel part 3. Thus, the entire



inner face 31a of reaction cell 31 serves as a cathode. Reaction cell 31 may be integrally formed with middle vessel part 3 or separately formed and fitted or otherwise incorporated into it. Thus, the inner face 31a of reaction  
5 cell 31 serves as a negative electrode to prevent corrosion by electrolysis.

Discharge electrode 41 is in the form of a rod having a diameter smaller than the inner diameter of reaction cell 31 and arranged at a predetermined position in such a  
10 manner that each one may be inserted into each reaction cell 31. The discharge electrode may be a cylindrically shaped mesh or net or a cylinder having an axial hollow.

In the present invention, the distance between the anode and the cathode is preferably equal. If this  
15 distance varies, an excessive current flows locally at narrow regions to accelerate deterioration of the anode at those regions. In this embodiment, inner wall 31a of reaction cell 31 preferably has a cylindrical shape. Preferably, the outer peripheral face of discharge  
20 electrode 41 also has a cylindrical shape so that the center axis of discharge electrode 41 substantially coincides with the center axis of inner wall 31a of reaction cell 31.

At an end of discharge electrode 41 is provided an  
25 insulating spacer 43 to prevent any contact with the inner face of reaction cell 31. Insulating spacer 43 is preferably formed to suit the shape of the outer surface of discharge electrode 41 and the shape of the inner face of

reaction cell 31. Insulating spacer 43 preferably has a through hole that allows the influent to pass.

Current feed terminal 42 is connected to a positive line 44, which is in turn connected to a positive terminal  
5 not shown of a constant dc source separately provided. Thus, discharge electrode 41 serves as an anode.

A chamber 7 is formed between the inner face of reaction cell 31 and discharge electrode 41 and connected to a discharge channel 8 formed at the connection between  
10 middle vessel part 3 and upper vessel part 4. Discharge channel 8 is connected to an outlet 34 at the upper end of middle vessel part 4 for discharging effluent from reaction vessel 1.

Thus, the reaction vessel in the hydrothermal  
15 electrolytic apparatus according to this embodiment has an inlet at the bottom for introducing an influent and an outlet at the top for discharging an effluent. This makes it easier to continuously hydrothermally electrolyze an influent. The reaction vessel has a plurality of rod-like  
20 discharge electrodes and the same number of reaction cells.

As used herein, the "volume of the chamber in the reaction cell" does not include the volume of discharge electrode 41 in reaction cell 31 but means the volume of the part where an influent is electrolyzed at high  
25 temperature and high pressure. In this embodiment, it specifically means the volume of chamber 7 located between electrodes 31a, 41 in reaction cell 31.

In this embodiment, the "overall surface area of a

pair of electrodes exposed in the chamber" means the total of the surface area of electrode 31a and the surface area of discharge electrode 41 exposed in chamber 7. This excludes the area of discharge electrode 41 not exposed in  
 5 chamber 7, eg, the surface area of the part of the discharge electrode located within upper vessel part 4 or the surface area of the part of the discharge electrode exposed in discharge channel 8 because these parts do not participate in the electrolysis of an influent.

10 Each member can be formed from any material so far as middle vessel part 3 and reaction cell 31 should be formed from an electrically conductive material and the reaction vessel as a whole should be formed from a heat-resistant and pressure-resistant material. For example, middle  
 15 vessel part 3 and reaction cell 31 can be formed from stainless steel. Reaction cell 31 may have a multilayer structure comprising the innermost layer of an electrically conductive material such as stainless steel and the other layers of ceramics.

20 The hydrothermal electrolytic apparatus according to this embodiment can be used as follows.

An influent is heated up to a subcritical temperature and then introduced via inlet 21. At the same time, an oxidizer such as oxygen-dissolved water is introduced via  
 25 oxidizer inlet 22 and mixed with the influent in mixing chamber 23. The influent mixed with the oxidizer is forced upward under the pressure of successively introduced influent and oxidizer and inserted into reaction cell 31

via lower opening 31b of reaction cell 31. The influent introduced into reaction cell 31 is subjected to hydrothermal reaction and electrolytic oxidation reaction as it moves in chamber 7 so that reducible substances in the influent are degraded. The treated influent is introduced into discharge channel 8 via upper opening 31c and discharged from outlet 34. The effluent after treatment is introduced into various tanks as in known processes. In the apparatus according to this embodiment, a series of these reaction processes can be continuously performed.

The hydrothermal electrolytic apparatus according to this embodiment has the advantage that a large amount of influent can be treated because the reaction vessel has electrodes of a specific area as described above, which increases the throughput and advances a homogeneous reaction. Moreover, this embodiment allows a large amount of influent to be continuously treated even using a reaction vessel having an inlet at the bottom and an outlet at the top because said electrodes have a specific area. This embodiment also has the advantage that current feed terminals are easily mounted to improve workability.

Therefore, the apparatus of the present invention improves the efficiency of hydrothermal electrolytic reaction to effectively use the input energy and also reduces the size of the apparatus by increasing the surface area of electrodes per volume of chambers.

Next, a second embodiment of the present invention is

explained with reference to Figs. 5-9, in which Fig. 5 is a longitudinal sectional view showing the inner structure of the reaction vessel forming the core of the hydrothermal electrolytic apparatus according to a second embodiment of the present invention, Fig. 6 is a widthwise sectional view showing the inner structure of the reaction vessel, Fig. 7 is an enlarged sectional view of E in Fig. 5, Fig. 8 is an enlarged sectional view of F in Fig. 6, and Fig. 9 is an enlarged sectional view of G in Fig. 5. In the following description, differences from the first embodiment are described especially in detail. The foregoing explanation about the first embodiment is appropriately applied when no special reference is made.

In the second embodiment shown in Figs. 5-9, lower vessel part 2 has an influent inlet 21 at the center of the bottom, and a pipe 26 is connected to inlet 21 to extend upward from lower vessel part 2 to middle vessel part 3. Influent has been preliminarily mixed with an oxidizer in a mixer not shown, if desired. Preferably, influent has been preliminarily heated up to a temperature of 100°C or more but the critical temperature or less.

Middle vessel part 3 includes an anode 35a and a cathode 35b. Anode 35a (first electrode) has two or more concentrically cylindrical side walls 37a (first side walls) and a connecting member 36a (first connecting member) for connecting side walls 37a together. In the same manner, cathode 35b (second electrode) has two or more concentrically cylindrical side walls 37b (second side

walls) and a connecting member 36b (second connecting member) for connecting side walls 37b together. Side walls 37a of anode 35a and side walls 37b of cathode 35b are alternately arranged to form a channel for influent between  
5 side walls 37a and 37b.

Preferably, pipe 26 is electrically connected to connecting member 36b to serve as cathode 35b. Thus, pipe 26 and the reaction vessel body can be protected against corrosion by cathodic protection.

10 Both connecting members 36a, 36b are in the form of a disk and electrically conductive. Connecting member 36a fixes anode 35a to current feed terminals 42. Connecting member 36b fixes cathode 35b to lower vessel part 2.

Thus, the hydrothermal electrolytic reactor according  
15 to this embodiment has a concentrically cylindrical continuous reaction channel. The reaction channel is continuously provided from the center to the outer periphery of the reaction vessel so that influent flows from the center to the outer periphery of the reaction  
20 vessel. Upper vessel part 4 includes a plurality of current feed terminals 42. Upper vessel part 4 and current feed terminals 42 are electrically insulated from each other via an insulator 42a, as shown in Fig. 9.

In this embodiment, the "volume of chambers in the  
25 reaction cell" means the volume of the part where the influent is hydrothermally electrolyzed in middle vessel part 3. The "volume of chambers in the reaction cell" excludes the volume of anode 35a, the volume of cathode 35b

and the volume defined by pipe 26.

When pipe 26 serves as a cathode, radially outer channels of pipe 26 are included in the chamber. When pipe 26 is not electrically conductive and does not serve as an electrode, however, radially outer channels of pipe 26 are not included in the chamber.

In the apparatus according to this embodiment, influent is introduced from inlet 21 and transferred to the top of the reaction vessel through pipe 26, then transferred from the top to the bottom of the reaction vessel in the outer channel, then transferred from the bottom to the top in the subsequent outer channel, and so on. Thus, it is transferred successively from the center to the periphery of the reaction vessel. During then, reducible substances in the influent are oxidatively degraded by hydrothermal electrolysis. The treated influent is discharged from outlet 34 to the outside of reaction vessel 1.

In addition to the same advantages as obtained in the first embodiment, the apparatus according to this embodiment also has the advantage that the reaction channel can be longer to improve the efficiency of electrolysis. Thus, even low-concentration influents can be effectively treated.

Hydrothermal electrolytic apparatus according to the first and second embodiments are not limited to the foregoing embodiments, but can be modified in various respects without departing from the spirit of the present

invention.

For example, a mixing chamber having a stirrer was illustrated in the first embodiment, but the mixing chamber may not be necessary as shown in the second embodiment.

- 5 The mixing chamber may not necessarily have a stirrer or a dispersion plate so far as the influent and oxidizer or the like are mixed.

The embodiment shown in Figs. 2 and 3 may be replaced by the embodiment shown in Figs. 10 and 11. That is, a  
10 heat-insulating material 39 may be filled outside reaction cell 31 in middle vessel part 3.

Alternatively, the reaction vessel may be thermally insulated by evacuation from a vacuum pump via a port formed in middle vessel part 3 instead of using an  
15 insulating material.

Alternatively, the temperature may be kept by providing a heater 45 on the outer peripheral face of middle vessel part 3 as shown in Fig. 12. Ports 46 and 47 may be further provided in middle vessel part 3 as shown in  
20 Fig. 12. Thus, the temperature can be kept constant by directly heating the inside of middle vessel part 3 with a thermal fluid flown from port 46 into middle vessel part 3. The thermal fluid is discharged from port 47. The thermal fluid may be used not only for heating but also cooling.

25 It is useful to provide a heater on the outer peripheral face of middle vessel part 3 as shown in Fig. 12 especially in the second embodiment in which the temperature of the influent may be lowered as it closes to



the peripheral face of the vessel.

Next, materials of members, reaction conditions or the like that can be used in the present invention are described. In hydrothermal electrolytic apparatus of the present invention, the discharge electrode or anode preferably has a surface having ruthenium, iridium, platinum, palladium, rhodium, tin or an oxide thereof or a ferrite. For example, the discharge electrode itself may be made from these materials. Alternatively, the base material of the discharge electrode may be coated with these materials on the surface.

Ruthenium, iridium, platinum, palladium, rhodium and tin may be elemental metals or oxides. Alloys of these metals are also preferably used. Such alloys include, for example, platinum-iridium, ruthenium-tin and ruthenium-titanium. These metals show high corrosion resistance, excellent insolubility for use as an anode. In some embodiments, especially preferred electrodes are based on palladium, ruthenium or an alloy of platinum and iridium.

During the hydrothermal electrolytic reaction of the present invention, the current density at the surface of the anode is preferably  $0.1 \text{ mA/dm}^2$  -  $500 \text{ A/dm}^2$ . If the current density is higher than  $500 \text{ A/dm}^2$ , the surface of the anode is liable to be exfoliated or dissolved. If the current density is lower than  $0.1 \text{ mA/dm}^2$ , however, the area of the anode must be increased and the system becomes bulky. The current density is more preferably  $10 \text{ mA/dm}^2$  -  $100 \text{ A/dm}^2$ , most preferably  $100 \text{ mA/dm}^2$  -  $50 \text{ A/dm}^2$ . If a new material

for the anode is developed, the current density at the anode can be further increased.

In hydrothermal electrolytic apparatus and processes of the present invention, an influent containing water and reducible substances can be treated to oxidatively degrade the reducible substances. Influent that can be treated by the present invention include various waste liquors. Reducible substances that can be degraded by the present invention include organics and ammonia. Examples of organics include aliphatic and aromatic hydrocarbons such as alkanes, alkenes, alkynes; alcohols; aldehydes; ketones; amines; carboxylic acids such as acetic acid; carboxylic acid derivatives such as esters, amides, anhydrides; halogenated hydrocarbons; phenols; sulfur-containing organic compounds such as sulfoxides, mercaptans, thiols, polysulfones; etc. Organics also include synthetic polymers such as polyolefins, polyesters or various engineering plastics.

Influent preferably have fluidity, and may be any of suspension, emulsion, aqueous solution or slurry, but preferably suspension or slurry. Influent may contain liquid or solid reducible substances. Influent include suspensions of unprecipitable solid particles dispersed in water, emulsions of liquid particles dispersed in water, aqueous solutions of liquid organics or inorganics dissolved in water and mixtures thereof. For example, influent contain a continuous phase containing water, liquid organics and dissolved salts and a discontinuous

phase containing solid organics such as particles, and optionally non-combustible solids such as ash.

Preferably, influents contain a strong acid ion. This is because strong acid ions show an electrochemical catalytic effect to advance hydrothermal electrolytic reaction more efficiently. The strong acid ion may be an inorganic acid ion or an organic acid ion. However, the strong acid is preferably an inorganic acid ion because organic acid ions may be degraded as hydrothermal electrolysis proceeds.

Suitable inorganic strong acid ions include, for example, halide ions, sulfate ion ( $\text{SO}_4^{2-}$ ), nitrate ion ( $\text{NO}_3^-$ ), phosphate ion ( $\text{PO}_4^{3-}$ ), among which halide ions are especially preferred. Suitable organic strong acid ions include, for example, trifluoroacetate ion ( $\text{CF}_3\text{COO}^-$ ).

Suitable halide ions include chloride ion ( $\text{Cl}^-$ ), bromide ion ( $\text{Br}^-$ ), iodide ion ( $\text{I}^-$ ) or any combination thereof, among which chloride ion or bromide ion is especially preferred. A halide ion-producing salt may be dissolved in the influent. A hydrohalic acid such as hydrogen chloride ( $\text{HCl}$ ), hydrogen bromide ( $\text{HBr}$ ) or hydrogen iodide ( $\text{HI}$ ) may be contained in the influent. When the influent contains polyvinyl chloride, chloride ion moves to the aqueous phase to incorporate chloride ion as hydrothermal reaction proceeds.

In hydrothermal electrolysis according to the present invention, an oxidizer is preferably added to the influent to more efficiently advance hydrothermal electrolytic

oxidation. Oxidizers that can be used in the present invention are oxygen gas, ozone gas, hydrogen peroxide and hypohalous acids, more preferably oxygen gas. Oxygen gas may be a gas containing oxygen gas, eg, air is preferably used. Thus, air can be bubbled into water or the like to dissolve oxygen, and the resulting oxygen-dissolved water can be introduced as an oxidizer via oxidizer inlet 22. Alternatively, compressed air can be introduced into reaction cell 23 to serve as an oxidizer.

10 In hydrothermal electrolysis according to the present invention, hydrothermal reaction takes place at a temperature of 100°C or more but the critical temperature of said influent or less and at a pressure that allows said influent to be kept in the liquid phase. Temperatures  
15 lower than 100°C are not preferred because the rate of hydrothermal reaction is lowered to extend the reaction time. However, the finding of the present invention cannot be directly applied for temperatures higher than the critical temperature because physical properties of aqueous  
20 medium significantly change. At the supercritical stage, for example, the solubility of the electrolyte greatly decreases and electric conductivity is decreased.

Next, a specific arrangement of an influent treatment system using a hydrothermal electrolytic reactor according to the present invention is explained with reference to Fig.  
25 13. Fig. 13 shows such an influent treatment system. In the treatment system shown in Fig. 13, an influent line 60 for supplying an influent is connected to a hydrothermal

electrolytic reaction vessel 1 of the present invention. Influent line 60 preferably has a feed tank 61, a high-pressure pump 66, a heat exchanger 70 and a heater 74, and an influent can be transferred in this order. Hydrothermal  
 5 electrolytic reaction vessel 1 may consist of a hydrothermal electrolytic reaction vessel according to the first embodiment, a hydrothermal electrolytic reaction vessel according to the second embodiment or the like.

Feed tank 61 can hold an influent. To feed tank 61  
 10 are connected a wastewater line 62 for introducing wastewater into feed tank 61 and a halide line 63 for supplying a halide ion source such as chloride ion ( $\text{Cl}^-$ ) into feed tank 61. This halide ion source may be sea water. Halide line 63 can supply a halide ion such as chloride ion  
 15 to feed tank 61 to control the halide ion level in the influent held in feed tank 61.

Feed tank 61 can be connected to high-pressure pump 66 via line 64 to transfer an influent. A tap water line 68 for supplying tap water is preferably connected to line  
 20 64 so that tap water substantially free from reducible substances can be transiently flown when the hydrothermal electrolytic apparatus shown in Fig. 13 is started up or stopped.

High-pressure pump 66 pressurizes the influent to a  
 25 pressure required for hydrothermal reaction to force the influent into reaction vessel 1 under this pressure via heat exchanger 70 and heater 74.

Influent line 60 preferably has heat exchanger 70.

Heat exchanger 70 is connected to influent line 60 and effluent line 100 so that heat exchanger 70 changes heat between the influent flowing in influent line 60 and the effluent flowing in effluent line 100. The influent  
5 pressurized in high-pressure pump 66 is often at room temperature. However, the effluent discharged from reaction vessel 1 is kept at high temperature via hydrothermal reaction. Therefore, heat exchanger 70 heats the influent flowing in influent line 60 and cools the  
10 effluent flowing in effluent line 100. Even if the heat exchanger is not provided, only heat efficiency decreases.

Preferably, influent line 60 has a heater 74 for further heating the influent heated by heat exchanger 70. Especially when reaction vessel 1 has a large diameter, it  
15 is inefficient to heat influent 52 in reaction vessel 1 from the outside of reaction vessel 1 and it is thus preferable to provide heater 74 in the influent line. Heater 74 heats the influent to a temperature required for hydrothermal reaction, for example. The temperature to  
20 which the influent is heated is determined taking into account the exothermic heat from the oxidation reaction and the exothermic heat from the electrolysis of reducible substances in reaction vessel 1. Another heater for heating the outside of reaction vessel 1 may be further  
25 provided.

Separately from influent line 60, an oxidizer line 80 is preferably provided. Suitable oxidizers include gases containing oxygen gas such as air. Air is introduced into

compressor 82 via line 81 and preferably pressurized from  
1 MPa to 25 MPa, for example. This compressed air is  
introduced into accumulator 84 via line 83. Thus,  
compressor-induced pulsation of compressed air can be  
5 prevented.

A valve 85 for controlling the amount of compressed  
air, ie, the amount of oxidizer is provided downstream of  
accumulator 84. Compressed air is preheated in heat  
exchanger 87 and then introduced into reaction vessel 150  
10 via line 188. Heat exchanger 187 heats compressed air and  
cools the effluent.

Alternatively, a liquid such as water in which oxygen  
gas is dissolved may be introduced into reaction vessel 1.  
Oxidizers in the form of a gas such as oxygen gas  
15 (including air) have higher water-solubility at lower  
temperature or higher pressure. Therefore, an oxidizer in  
the form of a gas may be dissolved in water at low or room  
temperature under high pressure and then this cold water  
may be supplied to the reaction vessel. Alternatively,  
20 aqueous hydrogen peroxide, a hypochlorous acid or a solid  
oxidizer may be dissolved in water and supplied to the  
reaction vessel via a high-pressure pump or the like. When  
an oxidizer rich in water is added, an additional heater  
may be provided between high-pressure pump 86 and reaction  
25 vessel 1.

Preferably, oxidizer line 80 is directly connected to  
reaction vessel 1. If oxidizer line 80 is connected to  
influent line 60, line 76 between heater 74 and reaction

vessel 50 will be susceptible to corrosion. On the another hand, when an oxidizer is directly introduced into reaction vessel 1, the inner wall of reaction vessel 1 can be protected from corrosion because the inner wall of reaction vessel 11 serves as a cathode of electrolysis.

Reaction vessel 1 may consist of a reaction vessel according to the first or second embodiment as described above. Preferably, reaction vessel 1 has an axially extending tubular shape, preferably a cylindrical shape.

Positive terminal 96 and negative terminal 97 of dc source 94 are connected to the anode and the cathode of hydrothermal electrolytic apparatus 1 via lines 98, 99, respectively.

In the embodiment shown in Fig. 13, an effluent line 100 for discharging the hydrothermally electrolyzed influent is connected to reaction vessel 1. Preferably, effluent line 100 has heat exchangers 70/87, a gas-liquid separator 102, and an effluent tank 110, and the effluent hydrothermally electrolyzed in reaction vessel 1 can be transferred in this order. Heat exchangers 70/87 have already been explained.

Preferably, gas-liquid separator 102 is connected to effluent line 100. Gas-liquid separator 102 separates gas and liquid in the effluent. The effluent is held at a predetermined level 104 in gas-liquid separator 102. Pressure transmitter tube may be provided between the space above said level 104 and the effluent below said level 104, and a level detector, for determining the gas-liquid



interface or slurry level, may be provided in this pressure transmitter tube. Level-detecting mechanism 106 may be designed to measure the level 104 by the pressure difference between gas and liquid to discharge the effluent in such a manner that said level 104 may be fixed or within a fixed range. Gas-liquid separator 102 may be provided with a piezoelectric element for converting pressure into an electric signal each above and below said level 104, whereby this electric signal is entered into a level detector to detect the pressure difference.

Preferably gas-liquid separator 102 has a level-controlling mechanism 106 stabilizing the level of the effluent in gas-liquid separator 102 within a fixed range. Said level-controlling mechanism may have a level detector for detecting the pressure difference between gas and the effluent, a valve for discharging the effluent and a controller for controlling the valve by a signal from the level detector. The level-controlling mechanism may have a pressure transmitter tube or a piezoelectric element.

A valve 108 is connected to gas-liquid separator 102 so that the effluent in gas-liquid separator 102 can be discharged into container 110 when valve 108 is opened. Preferably, switching of valve 108 is controlled by a signal from level-controlling mechanism 106.

Gas-liquid separator 102 may have a pressure controlling mechanism for controlling the pressure in the gas-liquid separator within a predetermined range. Said pressure controlling mechanism may have, for example, a

pressure detector for detecting the pressure of the gas phase, a valve for discharging gas and a controller for controlling the valve by a signal from the pressure detector. The pressure-controlling mechanism controls the pressure in the range that the influent is kept at the liquid phase and reaction vessel 1 and gas-liquid separator 102 are safely operated, for example. The pressure detector may have a piezoelectric element.

A valve 109 is connected to gas-liquid separator 102 so that the gas in gas-liquid separator 102 can be discharged to the atmosphere when valve 109 is opened. Preferably, switching of valve 109 is controlled by a signal from a pressure-controlling mechanism not shown.

Next, a hydrothermal electrolytic process using the hydrothermal electrolytic treatment system shown in Fig. 13 is explained.

Explanation begins with the operation at start-up. Suppose that no liquid has been introduced into reaction vessel 1 yet. Tap water is first introduced into influent line 60 from tap water line 68 at room temperature and atmospheric pressure. Tap water is transferred through heat exchanger 70, heater 74 and then reaction vessel 1 by high-pressure pump 66. After tap water is introduced into heater 74, heater 74 is activated to heat tap water. Thus heated tap water is discharged from reaction vessel 1 to effluent line 100 and then discharged into container 110 via gas-liquid separator 102.

After the system is stabilized, tap water supply from

the tap water line to influent line 60 is stopped and influent supply from feed tank 61 to influent line 60 is started. Halide ion level or other like of the influent are preliminarily controlled via halide line 63 or the like.

5 The influent is introduced into reaction vessel 1 while heating of the influent is continued in heater 74. An oxidizer is introduced into reaction vessel 1 via oxidizer line 80.

After the influent and oxidizer are introduced into  
10 reaction vessel 1, electrolysis is started. Thus, dc source 94 is turned on to supply dc to the anode and cathode of hydrothermal electrolytic apparatus 1. The influent kept in the liquid phase under high temperature and high pressure moves in reaction vessel 1, during which  
15 hydrothermal reaction and electrolysis proceed at the same time. The heating temperature of heater 74 is appropriately lowered because heat is generated with hydrothermal reaction and electrolysis.

The reaction time should be enough long for reducible  
20 substances in the influent to be oxidatively degraded, for example 1 second to 48 hours, preferably 1 minute to 24 hours. The reaction time is more preferably 5 hours or less, still more preferably 2 hours or less. The reaction time is adjusted in function of the volume of reaction  
25 vessel 1 and the feed flow rate of the influent.

When the reaction is to be stopped, the inflow from feed tank 61 to influent line 60 is stopped and tap water is introduced from the tap water line to influent line 60.

Oxidizer supply from oxidizer line 80 into reaction vessel 1 is also stopped. Then, the dc source is turned off to stop electrolysis. Then, the output of heater 74 is lowered so that the temperature of the influent flowing into reaction vessel 1 is gradually lowered.

According to the first and second embodiments of the present invention, influent can be efficiently treated by hydrothermal electrolytic reaction by increasing the surface area of electrodes in hydrothermal electrolysis, as has been described above.

However, it is not always easy to increase the surface area of electrodes as desired because the surface area of electrodes cannot be indefinitely increased in a limited space of the reaction vessel even by the above approach.

Thus, we also provide a process and an apparatus for substantially increasing the surface area of electrodes easily and inexpensively as alternatives to the foregoing embodiments.

Namely, we found that the surface area of electrodes can be substantially increased by incorporating electrically conductive particles into the influent, preferably suspending electrically conductive particles into the influent so that the conductive particles present in the influent can substantially serve as an electrode during the electrolysis of the influent.

The incorporation of electrically conductive particles into the influent means that the influent

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containing water and electrically conductive particles is located between the original cathode and the original anode in the hydrothermal electrolytic apparatus. When a dc voltage is applied across the original cathode and the original anode, individual conductive particles serve as an anode at the surfaces facing the original cathode and as a cathode at the surfaces facing the original anode under the effect of an electric field. Therefore, a current flows locally between the original cathode and the surfaces of individual conductive particles serving as an anode, and also a current flows locally between the original anode and the surfaces of conductive particles serving as a cathode. When two conductive particles are located in proximity to but without contact with each other and the cathodic surface of one conductive particle faces the anodic surface of the other conductive particle, for example, a current flows locally between the cathodic surface and the anodic surface. This also applies to more than two discrete conductive particles, in which case a current seems to flow between the cathodic surface of a conductive particle and the anodic surface of another conductive particle.

Thus, the current flowing between the original anode and the original cathode increases and the voltage across the original anode and the original cathode also increases when conductive particles exist in the influent as compared with when no conductive particles exist in the influent. Therefore, a large amount of electric power can be supplied to the influent to greatly improve the throughput and

process efficiency of the hydrothermal electrolytic apparatus without increasing the surface area of the original anode and the original cathode.

Accordingly, a third aspect of the present invention  
5 provides a hydrothermal electrolytic process comprising the step of subjecting an influent containing water, reducible substances and conductive particles to electrolysis at a temperature of 100°C or more but the critical temperature of said influent or less and at a pressure that allows  
10 water in said influent to be kept in the liquid phase.

In the third aspect of the present invention, said conductive particles are suspended in said influent, and said influent preferably further contains a strong acid ion. Preferably, said electrolysis step is followed by the step  
15 of separating said conductive particles and the step of adding the separated conductive particles to said influent again.

Still another aspect of the present invention provides a hydrothermal electrolytic apparatus comprising a  
20 feeder for supplying an influent containing water and reducible substances with conductive particles, and a reaction cell for subjecting said influent supplied with conductive particles to electrolysis at a temperature of 100°C or more but the critical temperature of said influent  
25 or less and at a pressure that allows water in said influent to be kept in the liquid phase. In said apparatus, said reaction cell preferably has a pair of electrodes, more preferably one of which serves as an anode and the

other serves as a cathode.

Still another aspect of the present invention provides a hydrothermal electrolytic apparatus comprising a reaction cell for supplying a direct current to an influent  
5 containing water, reducible substances and conductive particles at a temperature of 100°C or more but the critical temperature of said influent or less and at a pressure that allows water in said influent to be kept in the liquid phase, and a separator for separating the  
10 conductive particles from the effluent. Preferably, said reaction cell has a pair of electrodes, more preferably one of which serves as an anode and the other serves as a cathode.

In said hydrothermal electrolytic apparatus, said  
15 separator preferably comprises a liquid cyclone. Or said separator preferably comprises a filter device.

In the third aspect of the present invention, the influent contains conductive particles. When a dc voltage is applied across the original cathode and the original  
20 anode in a hydrothermal electrolytic apparatus supplied with a influent containing conductive particles, individual conductive particles serve as an anode at the surfaces facing the original cathode and as a cathode at the surfaces facing the original anode under the effect of an  
25 electric field. Therefore, a current flows locally between the original cathode and the surfaces of individual conductive particles serving as an anode, and also a current flows locally between the original anode and the

surfaces of conductive particles serving as a cathode.

When two conductive particles are located in proximity to but without contact with each other and the cathodic surface of one conductive particle faces the anodic surface of the other conductive particle, for example, a current flows locally between the cathodic surface and the anodic surface. This also applies to more than two discrete conductive particles, in which case a current seems to flow between the cathodic surface of a conductive particle and the anodic surface of another conductive particle.

Therefore, the surface area of electrodes can be substantially increased without increasing the surface area of the original anode and the original cathode.

Preferably, conductive particles are suspended in the influent. As a result, solid conductive particles can flow with the influent. This also prevents conductive particles from adhering to the surface of electrodes.

Conductive particles may be wholly formed of a conductive material. Alternatively, they may be particles of a conductive material coated with another conductive material on their surfaces or particles of a non-conductive material coated with a conductive material on their surfaces. Even particles having an insulating oxide or the like deposited on their surfaces by corrosion or other reasons are regarded as conductive particles so far as they are generally conductive.

Particles formed of a conductive material include, for example, carbon particles, metal particles and



conductive oxide particles. Carbon particles include, for example, particles of graphite. Metal particles include, for example, so-called metal powders such as iron powder, copper powder, silver powder, nickel powder, cobalt powder and aluminium powder. Conductive oxide particles include particles of a ferrite and ruthenium oxide. In terms of costs, iron powder and aluminium powder are preferred. Iron powder includes powdered scrap from machining of steel (including stainless steel), cast iron or the like.

10           Particles of a conductive material coated with another conductive material include metal particles coated with a thin film of another metal on their surfaces such as copper particles coated with platinum on their surfaces.

15           Particles of a non-conductive material coated with a conductive material on their surfaces include particles of an oxide powder coated with a metal thin film on their surfaces such as aluminium oxide particles coated with copper on their surfaces.

20           Particles of a conductive or non-conductive oxide powder coated with a conductive oxide on their surfaces are also suitable, such as zirconium oxide particles coated with iridium oxide on their surfaces and silicon dioxide particles coated with ruthenium oxide on their surfaces.

25           Synthetic polymer particles coated with a metal or a conductive oxide on their surfaces are also suitable, such as polymer particles of polyethylene glycol coated with ruthenium oxide on their surfaces.

Means for coating a metal thin film include

electroplating, electroless plating, sputtering, physical vapor deposition, chemical vapor deposition, etc. Means for coating a conductive oxide thin film include calcination, sputtering, physical vapor deposition, chemical vapor  
5 deposition, etc.

These conductive particles are subjected to a current in the presence of a strong acid ion such as a halide ion at high temperature and high pressure. Suitable conductive particles may be irreversible particles liable to be molten  
10 or corroded under these conditions or reusable chemically stable particles. For single use, iron powder, aluminium powder or the like are preferred in terms of costs. Reusable conductive particles preferably have such an excellent corrosion resistance that they remain insoluble  
15 even if a current is applied.

Reusable conductive particles are preferably formed of or coated with a conductive material having ruthenium, iridium, platinum, palladium, rhodium, copper, nickel, tin or an oxide thereof or a ferrite.

20 Ruthenium, iridium, platinum, palladium, rhodium, copper, nickel and tin may be elementary metals or oxides. Alloys of these metals are also preferably used. Such alloys include, for example, platinum-iridium, ruthenium-tin and ruthenium-titanium. In some embodiments,  
25 conductive materials based on palladium, ruthenium or an alloy of platinum and iridium are especially preferred.

Conductive particles may be in any form such as, but not limited to, sphere, rod, disk, T-shape, donut, tube,

fiber, etc. Hollow particles are also suitable.

Conductive particles preferably have a size shorter than the distance between the anode and the cathode. The average size of conductive particles is preferably 1 cm or less, more preferably 5 mm or less, still more preferably 1 mm or less, most preferably 0.5 mm or less. For example, the size of spherical conductive particles means their diameter. The size of rod-like or tubular conductive particles means their length. The size of conductive particles may be homogeneous or may widely vary.

Rod-like or tubular conductive particles preferably have an aspect ratio, ie, the ratio of the length to the diameter of the rod or tube of 0.1-1000, more preferably 0.5-100.

The influent preferably contains 0.01% by weight or more of conductive particles, more preferably 0.1% by weight or more of conductive particles. The presence of conductive particles in an amount even as small as 0.01% by weight in the influent increases a current, therefore a voltage across the original electrodes.

The influent preferably contains 30% by weight or less of conductive particles, more preferably 10% by weight or less of conductive particles. If more than 30% by weight of conductive particles are contained, the fluidity of the influent is affected and the probability of a short circuit between electrodes significantly increases.

The content of conductive particles in the influent means the content in the feed line for supplying the

influent into the reaction cell. This is because  
conductive particles are not always uniformly distributed  
in the reaction cell so that the content is difficult to  
exactly determine. When the reaction cell is tubular and  
5 the influent is transferred from the bottom to the top, for  
example, the concentration of conductive particles tends to  
be higher at the bottom of the reaction cell.

The third aspect of the present invention as defined  
above is explained in detail below with reference to Fig.  
10 14. In Fig. 14, elements having the same operation and  
function as those of the treatment system shown in Fig. 13  
are designated by the same reference numbers and not  
explained here.

In a hydrothermal electrolytic treatment system  
15 according to the third aspect of the present invention  
shown in Fig. 14, influent line 60 for supplying an  
influent is connected to reaction vessel 50. Influent line  
60 preferably has a feed tank 61, a high-pressure pump 66,  
a heat exchanger 70 and a heater 74, and an influent can be  
20 transferred in this order.

A feeder 130 for supplying conductive particles to  
feed tank 61 is provided. Feeder 130 comprises a hopper  
132 for holding conductive particles 138 and a screw feeder  
134 for quantitatively supplying conductive particles 138  
25 to feed tank 61. A motor 136 is connected to screw feeder  
134. The screw of screw feeder 134 rotates with the  
rotation of motor 136 to introduce a metered amount of  
conductive particles 138 into feed tank 61. Hopper 132 may

be supplied with crude conductive particles or conductive particles 112 separated by filter device 114. Feed tank 61 is equipped with a stirrer 61a for homogeneously agitating the influent.

5           Each member on influent line 60 has the same operation as explained about Fig. 13, and is not explained here.

10           Separately from influent line 60, an oxidizer line 80 is preferably provided. Each member on the oxidizer line also has the same operation as explained about Fig. 13, and is not explained here.

15           Preferably, reaction vessel 50 has an axially extending tubular shape, preferably a cylindrical shape. Reaction vessel 50 includes a pair of electrodes for electrolysis therein. Reaction vessel 50 has a metal inner wall 50s, which can serve as a cathode. For example, the wall of reaction vessel 50 may be wholly made from a metal. Reaction vessel 50 contains a rod-like anode 92 therein. Preferably, the outer face of anode 92 is also cylindrical so that the center axis of anode 92 substantially coincides with the center axis of reaction vessel 50. Anode 92 may be a cylindrically shaped mesh or net or a cylindrically shaped plate.

20           Positive terminal 96 and negative terminal 97 of dc source 94 are connected to anode 92 and cathode 50s via lines 98, 99, respectively. Line 98 for feeding the anode passes through the top 51b of reaction vessel 50, while line 98 is insulated from reaction vessel 50 by insulating

member 56. When reaction vessel 50 is made from a metal, line 99 may be directly connected to reaction vessel 50.

Reaction vessel 50 may be heated by a heater not shown. The heater may be an electric heater, for example.

5 The outside of the reaction vessel may be directly heated with a burner or the like.

In the treatment system shown in Fig. 14, a recycle line 120 for recycling conductive particles is connected to the reaction vessel. Recycle line 120 comprises a  
10 separator 122 for separating conductive particles from the effluent. Thus, conductive particles can be recycled without being discharged from the system.

Thus, a separator 122 for separating solid particles from the effluent is connected to the top of reaction  
15 vessel 50 via line 121. Separator 122 may consist of, for example, a liquid cyclone that centrifugally separates conductive particles. In the liquid cyclone, conductive particles settle at the bottom. In separator 122, all the conductive particles in the effluent may not be separated.  
20 Most of conductive particles may be removed in separator 122 and the remainder may be removed by filter device 110.

Separator 122 is connected to pump 126 via line 124, and pump 126 is connected to the bottom of reaction vessel 50 via line 127. When separator 122 consists of a liquid  
25 cyclone, a concentrated slurry containing conductive particles is obtained. This concentrated slurry can be introduced into the bottom of reaction vessel 50 by pump 126.

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An effluent line 100 for discharging the effluent deprived of at least a part of conductive particles is connected to separator 122. Effluent line 100 preferably has heat exchangers 87/70, a gas-liquid separator 102, and  
5 a filter device 110, and the effluent hydrothermally electrolyzed in reaction vessel 50 is transferred in this order.

Preferably, gas-liquid separator 102 is connected to effluent line 100. Gas-liquid separator 102 separates gas  
10 and liquid in the effluent. The effluent is held at a predetermined level 104 in gas-liquid separator 102. A pressure transmitter tube may be provided between the space above said level 104 and the effluent below said level 104, and a level detector for determining the gas-liquid  
15 interface or slurry level may be provided in this pressure transmitter tube. A level detecting mechanism not shown may be designed to measure the level 104 by the pressure difference between gas and liquid to discharge the effluent in such a manner that said level 104 may be fixed or within  
20 a fixed range. Gas-liquid separator 102 may be provided with a piezoelectric element for converting pressure into an electric signal each above and below said level 104, whereby this electric signal is entered into a level detector to detect the pressure difference.

25 Preferably gas-liquid separator 102 has a level-controlling mechanism 106 stabilizing the level of the effluent in gas-liquid separator 102 within a fixed range. Said level-controlling mechanism may have a level detector

for detecting the pressure difference between gas and the effluent, a valve for discharging the effluent and a controller for controlling the valve by a signal from the level detector. The level-controlling mechanism may have a pressure transmitter tube or a piezoelectric element.

A valve 108 is connected to gas-liquid separator 102 so that the treated water in gas-liquid separator 102 can be discharged into filter device 114 when valve 108 is opened. Preferably, switching of valve 108 is controlled by a signal from the level-controlling mechanism.

Gas-liquid separator 102 may have a pressure controlling mechanism for controlling the pressure in the gas-liquid separator within a predetermined range. Said pressure controlling mechanism may have, for example, a pressure detector for detecting the pressure of the gas phase, a valve for discharging gas and a controller for controlling the valve by a signal from the pressure detector. The pressure-controlling mechanism preferably adjusts the pressure at a level that allows filter device 114 to accomplish smooth separation, for example. The pressure detector may have a piezoelectric element.

A valve 109 is connected to gas-liquid separator 102 so that the gas in gas-liquid separator 102 can be discharged to the atmosphere when valve 109 is opened. Preferably, switching of valve 109 is controlled by a signal from a pressure-controlling mechanism not shown.

In the embodiment shown in Fig. 14, the pressure of gas-liquid separator 102 and the pressure of reaction



vessel 50 are preferably separately controlled so that the pressure of reaction vessel 50 is adjusted at a pressure that allows a liquid phase to be kept in hydrothermal electrolysis and the pressure of gas-liquid separator 102 is adjusted at a pressure that allows dielectric particles to be smoothly filtered by filter device 114.

For example, it is especially preferred that a pressure-regulating valve 115 having a pressure sensor is separately provided on line 100 to control the pressure of reaction vessel 50. Thus, the pressure of reaction vessel 50 is kept on the inlet side of valve 115, so that the pressure of reaction vessel 50 can be controlled via valve 115.

Filter device 114 filters the effluent to separate conductive particles 112 contained in the effluent. Filter device 114 may consist of a filter press, for example. The effluent deprived of conductive particles is stored in a container 116. On the other hand, these conductive particles 112 can be supplied to feeder 130 and recycled.

Next, a hydrothermal electrolytic process using the hydrothermal electrolytic treatment system shown in Fig. 14 is explained.

Feeder 130 supplies a desired amount of conductive particles 138 to feed tank 61 to control the content of conductive particles in the influent. A halide ion source is introduced from halide line 63 or the like into feed tank 61 to control its content. The influent is homogenized under agitation with stirrer 61a.

The influent in feed tank 61 is transferred by high-pressure pump 66, and the influent is preheated in heat exchanger 70 and further heated in heater 74, and then introduced into reaction vessel 50.

5        On the other hand, compressed air serving as an oxidizer is supplied via oxidizer line 80 and preheated in heat exchanger 87 and introduced into reaction vessel 50.

After the influent and oxidizer are introduced into reaction vessel 1, electrolysis is started. Thus, dc  
10        source 94 is turned on to supply dc to anode 92 and reaction vessel 50 serving as a cathode. The influent kept in the liquid phase under high temperature and high pressure moves from the bottom to the top in reaction vessel 50, during which hydrothermal reaction and  
15        electrolysis proceed at the same time to oxidatively degrade reducible substances in the influent. In the presence of a strong acid ion and conductive particles, dc can readily flow in the influent. The heating temperature of heater 74 is appropriately lowered because heat is  
20        generated with hydrothermal reaction and electrolysis.

The reaction time is enough long for reducible substances in the influent to be oxidatively degraded, for example 1 second to 48 hours, preferably 1 minute to 24 hours. The reaction time is more preferably 5 hours or  
25        less, still more preferably 2 hours or less. The reaction time is adjusted in function of the volume of reaction vessel 50 and the feed flow rate of the influent.

Effluent 52 is introduced into separator 122, where

conductive particles in the effluent are separated. Thus separated conductive particles are introduced with some amount of liquid into reaction vessel 50 by pump 126.

The effluent discharged from separator 122 is  
5 circulated through line 101, heat exchanger 87, line 102, heat exchanger 70 and valve 108 and introduced into gas-liquid separator 102.

Gas is discharged via valve 109, while liquid is introduced into filter device 110 via valve 107. Filter  
10 device 110 further removes conductive particles to discharge the effluent into container 116.

In the embodiment of the present invention shown in Fig. 14, a hydrothermal electrolytic apparatus according to the first and second embodiments of the present invention  
15 described with reference to Figs. 1-12 may be used as a hydrothermal electrolytic reactor. If a hydrothermal electrolytic apparatus having a plurality of reaction cells as shown in Figs. 1-12 is used to hydrothermally electrolyze an influent containing conductive particles,  
20 the efficiency of electrolytic reaction in hydrothermal electrolysis is further improved so that hydrothermal electrolytic treatment can be performed more efficiently. However, conductive particles contained in the influent here should have a size smaller than the distance between  
25 the anode and the cathode in each reaction cell.

The following examples illustrate a hydrothermal electrolytic apparatus according to the third aspect of the present invention without, however, limiting the present

invention thereto.

#### Example 1

Experiments were made using an autoclave shown in Fig. 15. The autoclave consists of a container body 200 made from SUS304 and a cover 201, and has an inner volume of 300 ml. An exhaust port 203 is formed in cover 201 and connected to an exhaust pipe 205 having a valve 204. The container also has a gas inlet 212 for introducing a purge gas.

A cylindrical platinum plate electrode 206 (outer diameter 26.5 mm, height 60 mm, effective area 50 cm<sup>2</sup>, initial dry weight 35.525 g) was provided in the autoclave. Although electrode 206 is shown as a net member, it was not a net but a plate in this example. Electrode 206 was connected to the positive electrode of outer power source 210, while cover 201 was connected to the negative electrode of the outer power source so that the inner wall face of the container body served as a cathode.

An artificial waste liquor consisting of 4,000 mg/L acetic acid (TOC 1,600 mg/L), 2 wt% NaCl and tap water was prepared. Spherical particles of silicon dioxide (glass beads) were coated with copper by electroless plating to prepare conductive particles. These conductive particles contain 5 wt% copper on the basis of the total weight of said conductive particles. These conductive particles had an average particle diameter of 0.2 mm. To 150 mL of said artificial waste liquor was added 5 g of said conductive particles.

At room temperature, 150 ml of said artificial waste liquor containing 5 g of conductive particles was introduced into the autoclave. Then, the autoclave was filled with argon in an amount equivalent to 3 MPa and sealed. Then, the content 220 was heated to 250°C by a heater 211 under agitation with a stirring impeller 202. When the temperature reached 250°C, application of a 6A constant dc current across electrodes was started and continued at 250°C for 15 minutes. During then, the average voltage was 7.50 V. After a lapse of 15 minutes, the application was stopped and the content was cooled to room temperature. After said conductive particles in the influent were settled, the supernatant was collected and analyzed.

This supernatant was colorless and odorless, and had a TOC of 30.4 mg/L. Thus, the TOC degradation reached 98.1%, showing tat the process of the present invention is very effective.

#### Comparative example 1

In this comparative example, the artificial waste liquor was treated under the same conditions as in the example above except that no conductive particles were added to the artificial waste liquor. When a 6A direct current was applied across electrodes, the average voltage was as low as 3.04 V. After treatment, the effluent showed a TOC of 954 mg/L with TOC degradation of only 40.3%.

Thus, the current flowing in the influent increases and the voltage across electrodes also increases when

conductive particles are suspended in the influent.

INDUSTRIAL APPLICABILITY

Hydrothermal electrolytic processes and apparatus according to various aspects of the present invention allow  
5 a large amount of waste liquor to be efficiently and continuously treated. Hydrothermal electrolytic apparatus of the present invention are well suitable for continuous processes, but also applicable to batch processes or semi-continuous processes.

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